Electronic Supplementary Information

Interconnected Assembly of ZrO₂@SiO₂ Nanoparticles with Dimensional Selectivity and Refractive Index Tunability

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School of Chemical Engineering and SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University (SKKU), Suwon 16419, Republic of Korea (1) TEM observation of ZrO2@SiO2 core-shell structures with dimensional variation



Figure S1. TEM images of aligned nanostructures of $ZrO_2@SiO_2$ with dimensional selectivity



Figure S2. HR-TEM observation of aligned nanostructures of $ZrO_2@SiO_2$ NPs.



(2) FT-IR characterization of surface-modified zirconia nanoparticles

Figure S3. FT-IR spectra of zirconia nanoparticles (black line) sequentially treated with nitric acid (red line), citric acid (blue line), and ammonium hydroxide (purple line).

FT-IR spectra data show that surface moieties of zirconia nanoparticles (NPs) were successfully switched by sequential functionalization processes. First, when ZrO_2 NPs were treated with nitric acid, the peak of hydroxyl groups emerged at ~3300 cm⁻¹ was identified. Then, citric acid was linked to hydroxyl group via coordinate covalent bonding, which was confirmed by the formation of -COO- (~1720 cm⁻¹) and -COH (~1420 cm⁻¹) group peaks. Finally, after treating with ammonium hydroxide, the OH and NH stretching vibrations provided from the ammonium salt were reflected by band broadening and band shifting toward the lower frequency at 3196 cm⁻¹. (3) Effect of concentration variation of ammonium hydroxide



Figure S4. TEM image of assembled zirconia NPs according to the concentration of ammonium hydroxide. (a) 0.14 M, (b) 0.7 M.

(4) Estimation of Hamaker constant of zirconia NPs under mixed solvents with varying the amount of ethanol

Table S1. Estimated Hamaker constants of zirconia NPs with different ethanol content.

Ethanol content	^E (dielectric constant)	refractive index (n)	Hamaker constant	
0 v/v	80.1	1.333	7.068 × 10 ⁻²⁰	
30 v/v	66.00	1.352	6.992 × 10 ⁻²⁰	
50 v/v	55.49	1.360	6.978 × 10 ⁻²⁰	
70 v/v	43.94	1.364	7.092 × 10 ⁻²⁰	
90 v/v	31.19	1.365	7.364 × 10 ⁻²⁰	

In this work, water/ethanol mixture is used as the dispersing medium, which can cause a change in the Hamaker constant according to the ethanol content. Theoretically, Hamaker constant of material (1) interacting with material (2) through a medium (3) can be calculated as:

$$A_{132} = \frac{3kT}{2} \sum_{n=0}^{\infty} \sum_{s=1}^{\infty} \frac{(\Lambda)^s}{s^3}$$
$$\Lambda = \left[\frac{\varepsilon_1(i\xi_n) - \varepsilon_3(i\xi_n)}{\varepsilon_1(i\xi_n) + \varepsilon_3(i\xi_n)} \right] \left[\frac{\varepsilon_2(i\xi_n) - \varepsilon_3(i\xi_n)}{\varepsilon_2(i\xi_n) + \varepsilon_3(i\xi_n)} \right], \ \xi_n = n(4\pi^2 kT/h)$$

k is the Boltzmann constant, h is Planck's

constant, T is temperature, ξ_n is an imaginary frequency, and $\varepsilon_{1,2,3}$ are the dielectric response function of materials 1, 2, and 3, respectively. Also, the imaginary dielectric response function, $\varepsilon(i\xi_n)$, can be represented by additively considering the terms contributed from microwave, UV, and IR relaxation regions, respectively. In particular, the microwave term is considered since at least 10 wt% of water is included in all cases.¹

$$\varepsilon(i\xi_{n}) = 1 + \frac{B_{micro}}{1 + (\xi/\omega_{micro})^{2}} + \frac{C_{IR}}{1 + (\xi/\omega_{IR})^{2}} + \frac{C_{UV}}{1 + (\xi/\omega_{UV})^{2}}$$

We assume that the absorption frequencies (ω_{IR} , ω_{UV} , ω_{micro}) in all regions rarely change. However, the value of B_{micro} might change in proportion to the variation of dielectric constant of the solution due to its dependency on the water content.

For example, when n = 0, C_{IR} and C_{UV} is calculated to be:

$$C_{\rm IR} = \varepsilon(0) - C_{\rm UV} - 1 - B_{\rm micro}$$

Also, C_{UV} is related to the refractive index in the visible region as follows:

$$C_{\rm UV} = n_{\rm vis}^2 - 1$$

For water: $\omega_{IR} = 6.22 \times 10^{14} \ rad \ s^{-1}$, $\omega_{UV} = 1.90 \times 10^{16} \ rad \ s^{-1}$, $\omega_{micro} = 1.08 \times 10^{11} \ rad \ s^{-1}$,

Meanwhile, for ZrO₂ (zirconia):² $\omega_{IR} = 1.88 \times 10^{14} rad s^{-1}$, $\omega_{UV} = 1.34 \times 10^{16} rad s^{-1}$.

(1) Renger, C.; Kuschel, P.; Kristoffersson, A.; Clauss, B.; Oppermann, W.; Sigmund, W. Colloid Probe Investigation of the Stabilization Mechanism in Aqueous 1,2-Propanediol Nano-Zirconia Dispersions. *Phys. Chem. Chem. Phys.* **2004**, 6, 1467–1474.

(2) Lennart, B. Hamaker Constants of Inorganic Materials. Advances in Colloid an interface science. 1997,

70, 125–169.

(5) Changes in zeta-potential values according to the ethanol content

 Table S2. Zeta-potential of zirconia NPs with different ethanol content.

Zeta-potential/ Ethanol contents	90 v/v	70 v/v	50 v/v	30 v/v	0 v/v
Without ammonia	-39 mV	-43 mV	-45 mV	-45 mV	-47 mV
With ammonia	-25 mV	-16 mV	-12.5 mV	-12.5 mV	

(6) Calculation of fractal dimension



Figure S5. TEM image of alignment structures of ZrO2@SiO2 core-shell-like particles according to the

variation of fractal dimension.

Ethanol	Total number	Average the number of	Average $R_{\rm g}$	Fractal	Standard
contents	of cluster	NPs in structure	(nm)	Dimension	deviation
95 v/v	32	83.5	46.9	1.34	0.070
70 v/v	32	91.5	34.5	1.52	0.121
50 v/v	32	107.5	24.0	1.81	0.098
30v/v	30	120.3	19.8	2.01	0.114

Table S3. Estimation of fractal dimension values with varying the mixing ratio of solvents

(7) Calculation of van der Waals attraction and electrostatic repulsion

$$\begin{split} V_T(r) &= V_{elec}(r) + V_{vdw}(r) \\ V_{elec}(r) &= 4\pi\epsilon_s\varepsilon_0 a^2 Y^2 \Big(\frac{kT}{e}\Big)^2 \frac{exp(-\kappa H)}{r} \\ Y &= \frac{8 \tanh\left(e\psi_0/4kT\right)}{1 + \left[1 - \frac{2\kappa a + 1}{(\kappa a + 1)^2} \tanh^2\left(e\psi_0/4kT\right)\right]^{1/2}} \\ \kappa &= \left[\frac{1000e^2 N_A(2I)}{\epsilon_s\varepsilon_0 kT}\right] \\ V_{vdw}(r) &= -\frac{A_H}{6} \left[\frac{2}{R^2 - 4} + \frac{2}{R^2} + \ln\frac{R^2 - 4}{R^2}\right] \end{split}$$

 $N_{\rm A} = 6.022 \times 10^{23}, e = 1.602 \times 10^{-19}, \varepsilon_0 = 8.854 \times 10^{-12}, k = 1.38 \times 10^{-23},$

T = 298K, $\alpha = 5.0$ nm, H = Debye length $\times 2$

Dimension	Dielectric constants	Ionic strength	Zeta- Potential (mV)	Debye length (nm)	van der Waals (1/kT)	Electrostatic (1/kT)	V _{vdw} / V _{elec}
1.34	28.3	0.0066	-25.0	2.24	-0.130	0.110	1.18
1.52	43.9	0.0108	-16.0	2.18	-0.140	0.071	1.97
1.81	55.5	0.0141	-12.5	2.15	-0.145	0.055	2.65
2.01	66.0.	0.0174	-12.5	2.11	-0.152	0.066	2.30
3D	28.3	0.0066	-10.0	2.24	-0.130	0.039	7.64

Table S4. Calculation of energy according to the competitive interactions between vdW attraction and electrostatic repulsion.